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Partial phase transitions in magnetocaloric material MnFe(P,As)

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Introduction

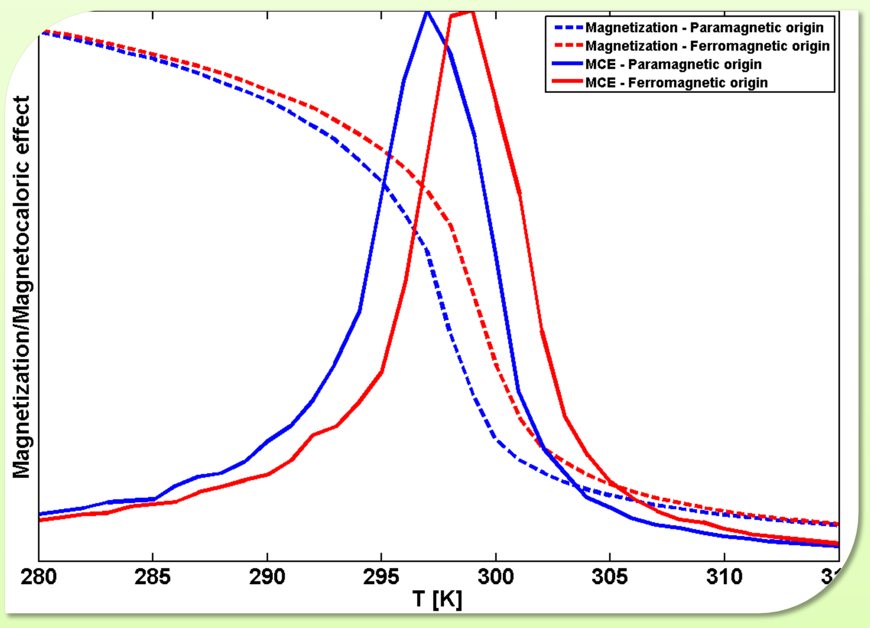
The field of magnetic refrigeration has grown a lot with the discovery of room temperature 1st order Magnetocaloric Materials (MCM), experiencing a large Magnetocaloric Effect (MCE). MCM are applied in Active Magnetic Regenerators (AMR), where they undergo thermodynamic cycles in order to heat or cool a system. This process has previously been modeled for 2nd order materials, but there is a general lack of detailed modeling of 1st order materials, where hysteresis is present [Nielsen et al.,2011].

We investigate how thermal hysteresis affects the heat capacity of the 1st order material MnFe(P,As) under partial phase transitions through Differential Scanning Calorimetry (DSC) and compare to a Preisach-type model.

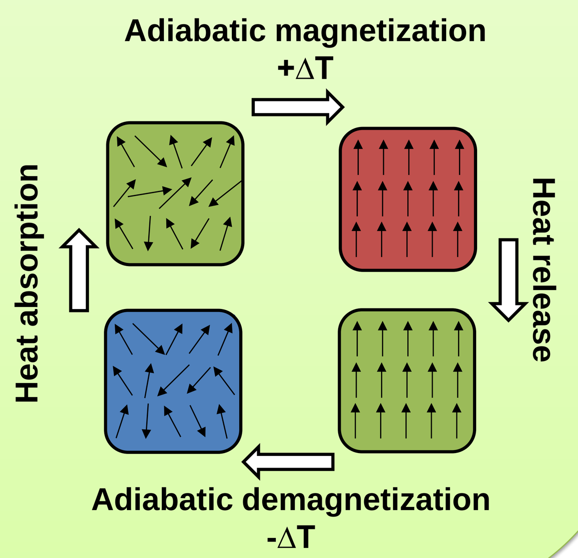
Magnetocaloric materials and magnetic refrigeration

The magnetocaloric effect can be measured as the adiabatic temperature change in magnetic material when a magnetic field is applied. Under adiabatic conditions the total entropy remains constant and the decrease of magnetic entropy is balanced by an increase in lattice entropy and a temperature increase. See Smith et al., 2011 for a review.

$$\Delta T_{ad}(T,H) = -\int_{H_0}^{H_1} \frac{T}{c(T,H)}\bigg|_H \frac{\partial M(T,H)}{\partial T}\bigg|_H dH$$



The magnetic refrigeration cycle
The MCE can be magnified by applying MCM in thermodynamic cycles, analogous to gas vapor-compression.



1st order materials

- Coupled structural and magnetic transition
- Large MCE! Wanted!
- Hysteresis… not wanted.

MnFe(P,As)

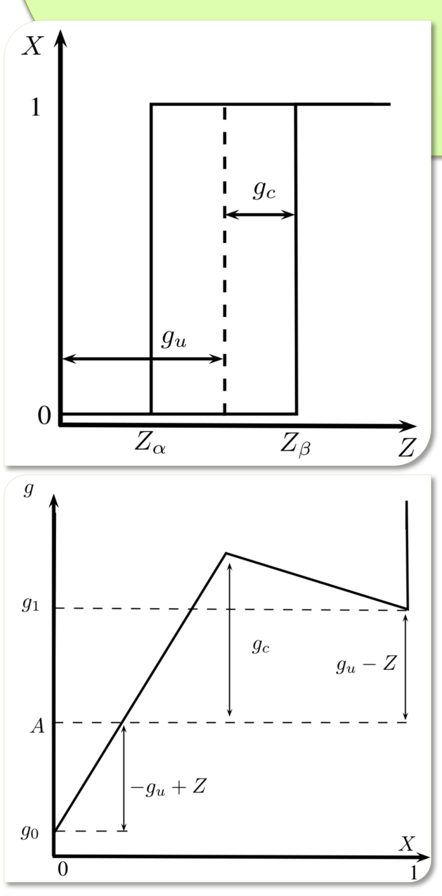
- 1st order material with a hexagonal Fe_2P structure.
- Phase transition between the low temperature ferromagnetic state and the high temperature paramagnetic state.
- The phase transition is magnetoelastic: at the transition temperature the c/a ratio of the hexagonal unit cell changes while the volume basically does not change [Dũng, 2012].

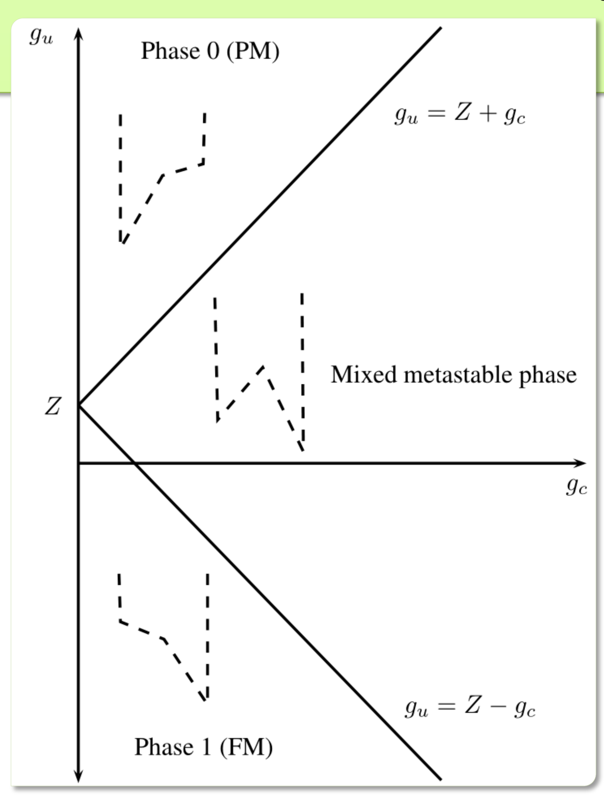
The Preisach-model

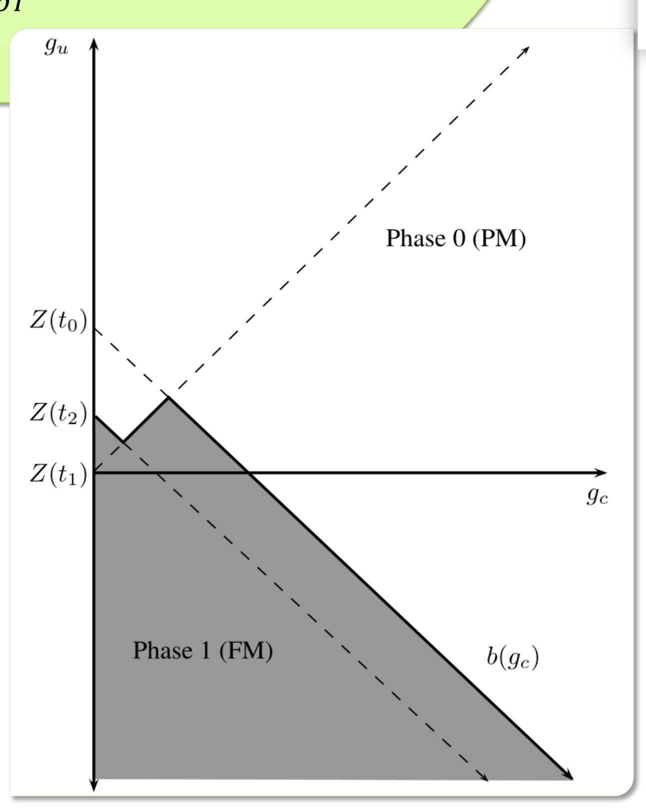
MCM behavior is often described by a set of *M(T,H)* and *c(T,H)* measurements. However, the applicability of such measurements in models is not straightforward when hysteresis is present.
Here we apply a Preisach-type model that is appropriate to describe the out-of-equilibrium thermodynamic aspects of hysteresis [Basso et al., 2007].

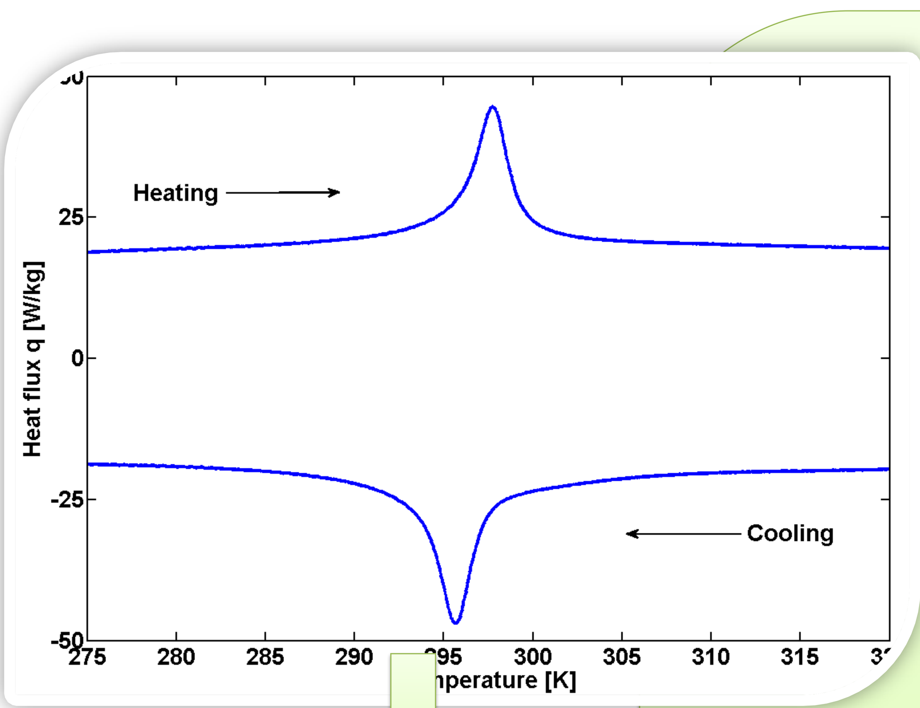
Modeling hysteretic behavior

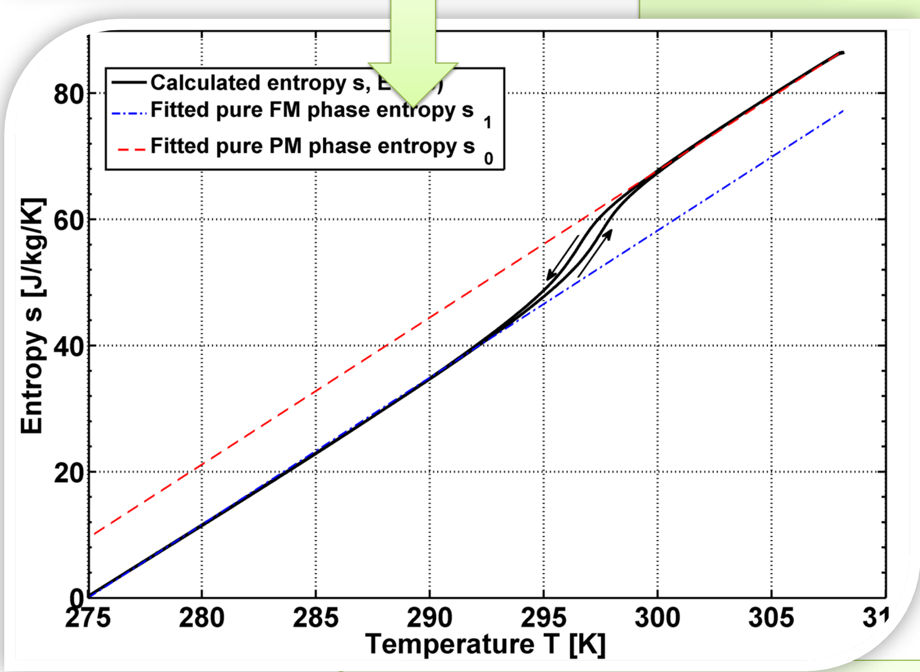
- A distribution, $p(g_u, g_c)$, of bistable hysteretic units, which can be either in phase 1 (ferromagnetic) or 0 (paramagnetic).
- Each unit is represented by parameters (g_u, g_c) which determine the critical phase switching fields
$$Z_\alpha = g_u - g_c\,, \qquad Z_\beta = g_u + g_c$$
- The difference in the Gibbs potential between phase 0 and 1 is the driving force in the transition
$$Z(T,H) = \frac{g_0(T,H) - g_1(T,H)}{2}$$
- History of *Z*-field determines the transition line *b(g_c)*, which gives the current ferromagnetic phase fraction
$$X_1 = \int_0^{+\infty} dg_c \int_{-\infty}^{b(g_c)} p(g_u, g_c) dg_u$$
- The phase fraction gives the relevant thermodynamic quantities of the mixed phase state, utilizing the pure phase material properties, e.g. entropy and heat flux
$$s = (1 - X_1)s_0 + X_1 s_1\,, \qquad q = T\frac{\partial T}{\partial t}\frac{\partial s}{\partial T}$$











Material modeling

Setting the scale
The entropy is estimated through heat flux measurements,

$$s(T) = \frac{1}{m}\int_{T_0}^{T} \frac{1}{\dot{T}'}\frac{q}{T'}dT' + s(T_0)$$

where the Gibbs free energy follows from

$$\frac{\partial g}{\partial T} = -s$$

The pure phase entropies are seen to be approximately linear

$$s_0(T) = c_b(T - T_{min}), \qquad s_1(T) = s_0(T) + \delta s$$

The right mix of hysteretic units
The Preisach distribution is assumed to have both a reversible and irreversible component

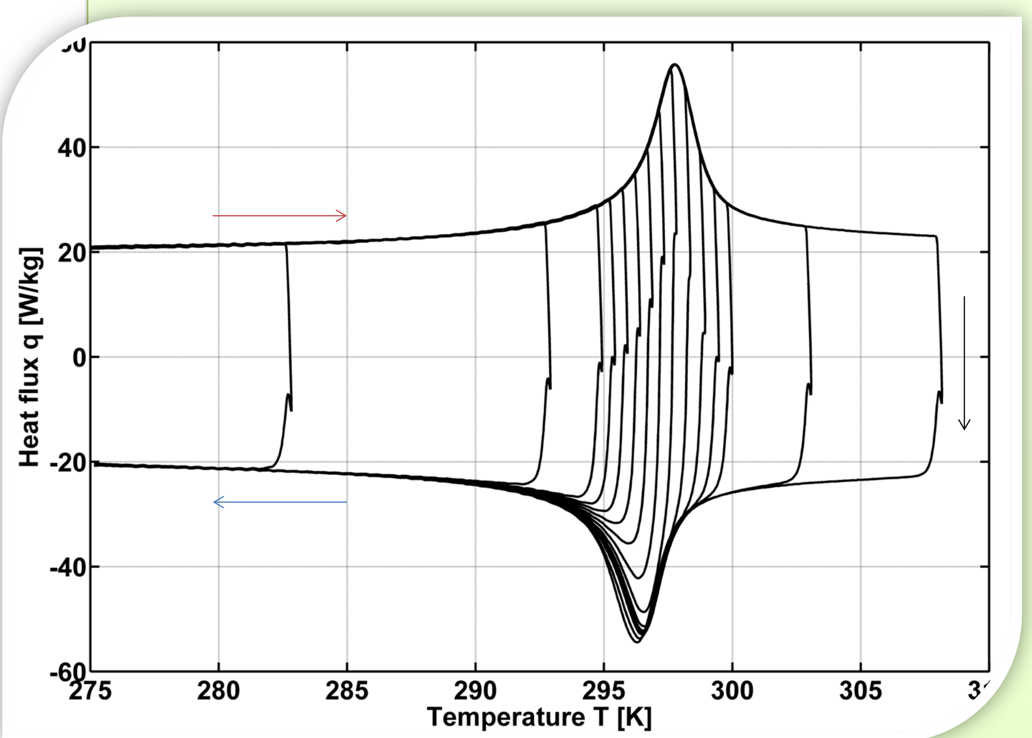
$$p_r(g_u, 0) \propto \exp\left(-\frac{g_u{}^2}{2\sigma_u{}^2}\right)$$

$$p_i(g_u, g_c) \propto \frac{1}{1 + \left(\frac{g_u}{\sigma_u}\right)^2}\,\frac{1}{1 + \left(\frac{g_c - g_{c,0}}{\sigma_c}\right)^2}$$

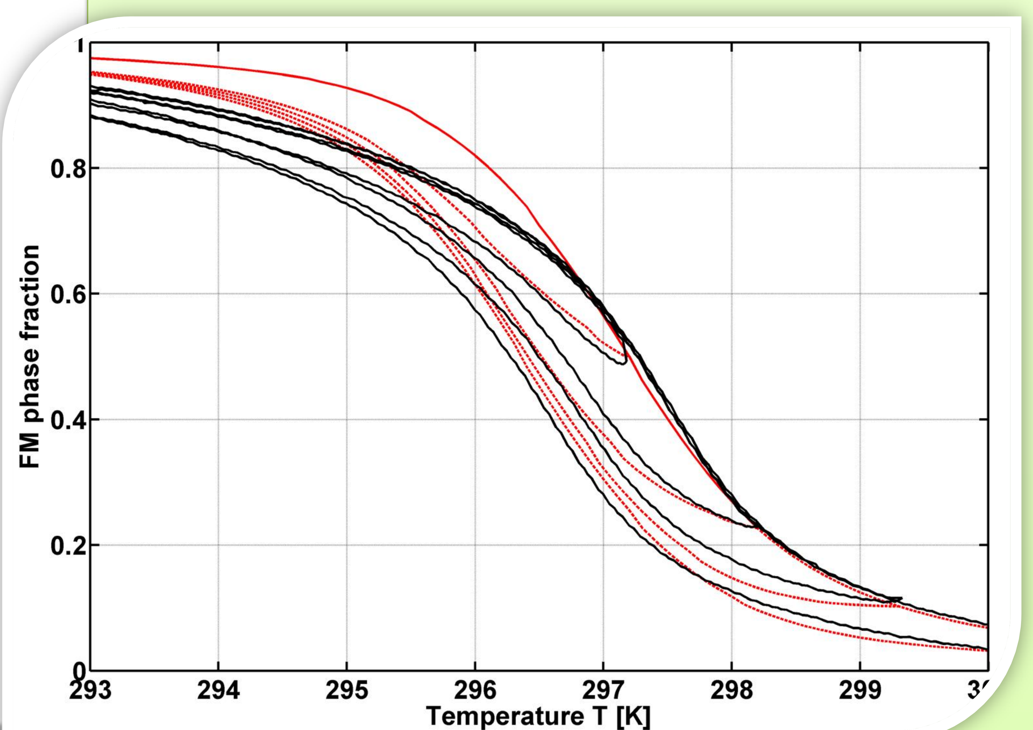
with $g_{u,0}$, $g_{c,0}$, σ_u and σ_c being material fitting parameters.

DSC measurements and model simulations

A 35 mg sample of MnFe(P,As) with T_C=296 K was measured with a commercial PerkinElmer Diamond DSC in 0 T magnetic field. The data is given as the heat flux *q* absorbed by the sample to maintain a constant temperature rate of ±2 K/min.



Measurements were performed with the sample originating in the FM phase. The sample was heated to a number of set temperatures, after which it was cooled again, resulting in partial phase transitions as shown in the figure.



The experimental FM phase fraction is obtained from the data as

$$X_{est}(T) = \frac{s - s_0}{s_1 - s_0}$$

and is shown as the solid black curve.

The experimental procedure was simulated with the Preisach model and the calculated FM phase fraction X_1 is shown as the dashed red curve

Results

- Model simulations generally fit well with complete transitions curves
- Transition not completely symmetric
- Model predictions of partial transitions lack detail and overestimate hysteresis → more detailed Preisach distribution
- Experimental data on partial phase transitions is needed to realistically model 1st order materials and the effect of hysteresis in AMR cycles

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